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Photosensitive Composition for Volume Hologram Recording

Technical Field

[0001]

The present invention relates to a photosensitive composition suitable for recording a volume hologram.

Background Art

[0002]

A volume hologram is produced in such a manner that objective light and reference light which is high in coherence and equal in wavelength are interfered to enter a hologram recording portion comprising a volume hologram recording material, and three-dimensional information regarding an object is recorded inside of a recording material layer as an interference fringe. The interference fringe is recorded, for example, as a refractive index modulation corresponding to the brightness and darkness of the interferential light. The volume hologram is widely utilized in the field of, for example, design use, security use, optical element use or the like since the volume hologram can three-dimensionally express a recorded subject, has high diffraction efficiency and wavelength selectivity, and requires advanced manufacturing technique or the like.

As a photosensitive composition for recording the volume hologram, there may be mentioned conventional materials such as silver salt and dichromated gelatin. These materials are

excellent in hologram recording performance; however, they are not preferable for mass-production since operation is cumbersome due to wet development, storage stability is inferior, or the like.

[0003]

Dry developing type photopolymer material can make it easier to produce a hologram than the case of using wet developing material, so that the development of dry developing type photopolymer material has been promoted in recent years. As the dry developing type photopolymer material, OmniDex series manufactured by DuPont is commercially available in mass-production level. The material contains a radical polymerizable monomer, a binder resin, a photoradical polymerization initiator and a sensitizing dye as main components, and can record a volume hologram by utilizing a refractive index difference between the radical polymerizable monomer and the binder resin (for example, see Patent Literature 1).

Also, materials using of both radical polymerization and cationic polymerization have been reported. For example, Patent Literature 2 discloses a system using a monomer having a diarylfluorene skeleton as a radical polymerizable monomer having a high refractive index and a cationic polymerizable monomer having a smaller refractive index than the radical polymerizable monomer. In the system, a high refractive index component polymerizes by radical polymerization upon interference exposure, and then an image is fixed by cationic

polymerization upon fixing exposure.

[0004]

Also, materials utilizing cationic polymerization are disclosed in, for example, the description of Patent Literature 3, etc. The materials are advantageous in that there is no oxygen inhibition in a radical polymerization system.

As a light source which has high coherence and is used for the volume hologram recording, a visible laser light is used. To increase the photosensitivity of the volume hologram recording material to the visible laser light, generally, the material is mixed with a so-called sensitizing dye which can sensitize the material to the wavelength of the visible laser light. As the sensitizing dye useful for volume hologram recording, there may be mentioned dyes disclosed in, for example, Patent Literatures 4, 5 and 6. Also, a combination of a sensitizing dye with a photopolymerization initiator is disclosed in Patent Literatures 7 and 8, for example.

[0005]

However, sensitivity upon interference exposure and hologram recording performance are not always exhibited as they are expected, and often can be just known by actually recording a hologram using a visible laser light individually and specifically adopted. Hence, it takes a lot of trouble to select a recording material and determine a recording condition.

[0006]

Patent Literature 1: Japanese Patent No. 2,664,234

Patent Literature 2: Japanese Patent No. 2,873,126

Patent Literature 3: U.S. Patent No. 5,759,721

Patent Literature 4: Japanese Patent Application

Laid-Open (JP-A) No. Hei. 5-27436

Patent Literature 5: JP-A No. Hei. 6-324615

Patent Literature 6: JP-A No. Hei. 7-281436

Patent Literature 7: JP-A No. 2000-109509

Patent Literature 8: JP-A No. 2000-109510

Disclosure of Invention

Problems to Be Solved by the Invention

[0007]

The present invention has been achieved in light of the above-stated conventional problems. An object of the present invention is to provide a volume hologram recording material wherein the composition is adjusted in accordance with an individually and specifically determined recording wavelength in the visible region and is excellent in sensitivity or hologram recording performance.

Means for Solving the Problems

[0008]

A photosensitive composition for volume hologram recording which is provided by the present invention to achieve the above object comprises a photopolymerizable compound as a

refractive index modulation component, a photopolymerization initiator and a sensitizing dye which increases the sensitivity of the photopolymerization initiator with respect to a wavelength in the visible region, wherein the sensitizing dye has a maximum absorption wavelength deviating by 14 nm or more from a predetermined volume hologram recording wavelength in the visible region, and the composition itself absorbs at the predetermined volume hologram recording wavelength.

The sensitizing ability of the sensitizing dye can be fully ensured by adjusting the composition of the photosensitive composition for hologram recording so as to satisfy, upon interference exposure using a recording wavelength in the visible region, the above certain relationship with an individually and specifically predetermined recording wavelength. Hence, excellent sensitivity or hologram recording performance can be obtained.

[0009]

The photosensitive composition for volume hologram recording of the present invention can further contain a binder resin and/or a thermosetting compound. By adding a binder resin, the photosensitive composition can be more easily utilized as a dry developing type hologram forming material. Also, a hologram recording portion which comprises the photosensitive composition for volume hologram recording that contains a thermosetting compound is fixed by a heat treatment after interference exposure, and a cationic polymerizable compound

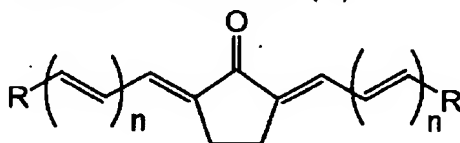
is crosslinked therewith due to a strong acid generated upon the interference exposure, thereby increasing the refractive index of the hologram recording portion, and thus enhancing refractive index modulation. Also, due to the resulting crosslinked structure, it is highly effective in increasing mechanical strength and resistance properties such as heat resistance and weather resistance.

[0010]

As the sensitizing dye of the photosensitive composition for volume hologram recording, a cyclopentanone skeleton containing compound represented by the following general formula (1) is preferably used:

[0011]

General formula (1):



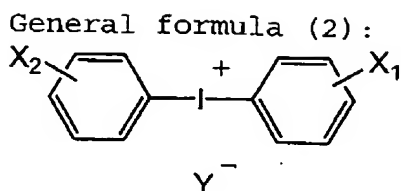
[0012]

wherein, "R" is a carbon-nitrogen containing substituent represented by "N_xC_y" in which x=1 to 4, y=8 to 30; "R" may contain a hydrogen atom and/or a halogen atom; and "n" is an integer of 0 to 3.

[0013]

Furthermore, as the photopolymerization initiator, a compound containing diaryliodonium skeleton represented by the following general formula (2) is preferably used:

[0014]



[0015]

wherein, each of "X₁" and "X₂" is independently an alkyl group having 1 to 20 carbons, halogen or an alkoxyl group having 1 to 20 carbons; and "Y⁻" is a monovalent anion.

[0016]

Furthermore, the photopolymerizable compound is preferably at least one kind selected from the group consisting of a photoradical polymerizable compound and a photocationic polymerizable compound.

[0017]

Furthermore, the photosensitive composition for volume hologram recording can further contain a second refractive index modulation component having a different refractive index from that of the photopolymerizable compound. When the photopolymerizable compound as a first refractive index modulation component is combined with the second refractive index modulation component, the refractive index difference between a strongly exposed portion and a weakly exposed portion can be increased upon exposure by the volume exclusion effect.

[0018]

In a preferred embodiment of the present invention, a photosensitive composition for volume hologram recording using a sensitizing dye which has a maximum absorption wavelength

deviating by 14 nm or more from a predetermined volume hologram recording wavelength in the region of 514 nm to 560 nm (green region) is provided. High diffraction efficiency can be obtained in the case of producing a green hologram by using the composition.

In a preferred embodiment of the present invention, a volume hologram having a diffraction efficiency of 80% or more can be obtained by using the photosensitive composition for volume hologram recording.

Effect of the Invention

[0019]

According to the composition for hologram recording of the present invention and a method of hologram recording using the composition, the sensitizing ability of the sensitizing dye can be fully ensured by adjusting the composition of the composition for hologram recording so as to satisfy, upon interference exposure using a recording wavelength in the visible region, the above certain relationship with an individually and specifically determined recording wavelength. Hence, excellent sensitivity or hologram recording performance can be obtained.

[0020]

According to the present invention, the diffraction efficiency or refractive index modulation amount Δn can be enlarged, and a visually bright and excellent hologram can be

formed. Thus, for example, a volume hologram having a diffraction efficiency of 80% or more, preferably 90% or more, can be produced.

Best Mode for Carrying Out the Invention

[0021]

Hereinafter, the present invention will be explained in more detail. In the present description, "(meth)acrylate" represents acrylate and methacrylate; "(meth)acryl" represents acryl and methacryl; and "(meth)acryloyl" represents acryloyl and methacryloyl.

[0022]

A photosensitive composition for volume hologram recording provided by the present invention (hereafter it may be referred to as "a composition for hologram recording") has a composition comprising, as essential components, a photopolymerizable compound as a refractive index modulation component, a photopolymerization initiator and a sensitizing dye which increases the sensitivity of the photopolymerization initiator with respect to a wavelength in the visible region, wherein the sensitizing dye has a maximum absorption wavelength deviating by 14 nm or more from a predetermined volume hologram recording wavelength in the visible region, and the composition itself absorbs at the predetermined volume hologram recording wavelength.

[0023]

Even if the recording wavelength of a laser light that is used for the interference exposure is consistent with the maximum absorption wavelength of the sensitizing dye that is contained in the composition for hologram recording, the sensitizing ability of the sensitizing dye cannot be fully exhibited.

To the contrary, in the present invention, the sensitizing ability of the sensitizing dye can be fully ensured by adjusting the composition of the composition for hologram recording so as to satisfy, upon interference exposure using a recording wavelength in the visible region, the above certain relationship with an individually and specifically determined recording wavelength. Hence, excellent sensitivity or hologram recording performance can be obtained.

[0024]

Therefore, by using a sensitizing dye which has a maximum absorption wavelength deviating by 14 nm or more from a recording wavelength in the red region (630 to 670 nm), a composition suitable for producing a red hologram can be obtained. By using a sensitizing dye which has a maximum absorption wavelength deviating by 14 nm or more from a recording wavelength in the green region (514 to 560 nm), a composition suitable for producing a green hologram can be obtained. By using a sensitizing dye which has a maximum absorption wavelength deviating by 14 nm or more from a recording wavelength set in the blue region (420 to 488 nm), a composition suitable for producing a blue hologram

can be obtained.

[0025]

The maximum absorption wavelength of the sensitizing dye shifts according to a solvent for dissolving the sensitizing dye to prepare a measuring sample or other components which coexist in the measuring sample. Hence, in the present invention, the maximum absorption wavelength of the sensitizing dye in the actually prepared composition for hologram recording is measured. If the composition for hologram recording is prepared in the state of a coating liquid using a solvent, the maximum absorption wavelength of the sensitizing dye is measured in the state that the composition for hologram recording is dried and contains no solvent.

[0026]

Also, the absorption wavelength of the composition for hologram recording shifts according to the solvent for dissolving the composition. Hence, in the state of containing no solvent, the composition for hologram recording is confirmed whether to absorb at the recording wavelength.

[0027]

The sensitizing dye is selected from the sensitizing dyes which can convert the radiation energy of a recording light having a wavelength in the visible region into the activation energy of the photopolymerization initiator. The above sensitizing dye is not particularly limited if the maximum absorption wavelength deviates from an individually and specifically

adopted recording wavelength by 14 nm or more to the high wavelength side or low wavelength side.

[0028]

It is, however, necessary for the composition for hologram recording of the present invention to absorb at the recording wavelength when the composition itself is measured for the absorption spectrum in the state of containing no solvent. The absorption of the composition at the recording wavelength is a total absorption of the compounded components including the sensitizing dye, the photopolymerization initiator, and so on. However, in many cases, the sensitizing dye makes a significant contribution. Therefore, as the sensitizing dye, one which absorbs at the recording wavelength is preferable, and one which absorbs well at the recording wavelength is more preferred.

[0029]

As the sensitizing dye, for example, there may be mentioned a cyanine dye, a melocyanine dye, a coumarin dye, a ketocoumarin dye, a cyclopentanone dye, a cyclohexanone dye, a thiopyrillium salt dye, a quinoline dye, a styrylquinoline dye, a thioxanthene dye, a xanthene dye, an oxonol dye, a rhodamine dye, a pyrillium salt dye or the like.

[0030]

Specific examples of the cyanine or melocyanine dye include 3,3'-dicarboxyethyl-2,2'-thiocyanine bromide, 1-carboxymethyl-1'-carboxyethyl-2,2'-quinocyanine bromide, 1,3'-diethyl-2,2'-quinothiacyanine iodide,

3-ethyl-5-[(3-ethyl-2(3H)-benzothiazolidene)ethylidene]-2-thioxo-4-oxazolidine, etc.

[0031]

Specific examples of the coumarin or ketocoumarin dye include 3-(2'-benzoimidazole)-7-diethylaminocoumarin, 3,3'-carbonylbis(7-diethylaminocoumarin), 3,3'-carbonylbiscoumarin, 3,3'-carbonylbis(5,7-dimethoxycoumarin), 3,3'-carbonylbis(7-acetoxycoumarin), etc.

[0032]

Specific examples of the cyclohexanone dye include 2,6-bis(4-dimethylaminobenzylidene)cyclohexanone, 2,6-bis(4-diethylaminobenzylidene)cyclohexanone, 2,6-bis(4-dimethylaminocinnamylidene)cyclohexanone, 2,6-bis(4-diethylaminocinnamylidene)cyclohexanone, 2,6-bis(4-N-ethyl-N-carbomethoxymethylaminobenzylidene)cyclohexanone and a sodium salt thereof, 2,6-bis(4-N-methyl-N-cyanoethylaminobenzylidene)cyclohexanone, 2,6-bis(4-N-ethyl-N-chloroethylamino cinnamylidene)cyclohexanone, etc.

[0033]

Specific examples of the cyclopentanone dye include 2,5-bis(4-dimethylaminobenzylidene)cyclopentanone, 2,5-bis(4-diethylaminobenzylidene)cyclopentanone, 2,5-bis(4-dibutylaminobenzylidene)cyclopentanone, 2,5-bis[(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolidine-9-

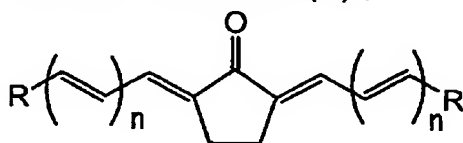
yl)methylene]cyclopentanone, 2,5-bis[2-(1,3,3-trimethyl-1,3-dihydro-2(2H)-indolinylidene)ethylidene]cyclopentanone, 2,5-bis[2-(1-ethyl-2(1H)-naphtho[1,2-d]thiazolinylidene)ethylidene]cyclopentanone, 2,5-bis(4-dimethylamino cinnamylidene)cyclopentanone, 2,5-bis(4-N-ethyl-N-carbomethoxymethylaminobenzylidene)cyclopentanone and a sodium salt thereof, 2,5-bis(4-N-methyl-N-cyanoethylamino benzylidene)cyclopentanone, 2,5-bis(4-N-ethyl-N-chloroethyl aminocinnamylidene)cyclopentanone, etc.

[0034]

Particularly, as the cyclopentanone dye, a cyclopentanone skeleton containing compound represented by the following general formula (1) is preferable:

[0035]

General formula (1):



[0036]

wherein, "R" is a carbon-nitrogen containing substituent represented by "N_xC_y" in which x=1 to 4, y=8 to 30; "R" may contain a hydrogen atom and/or a halogen atom; and "n" is an integer of 0 to 3.

[0037]

Specific examples of the compound represented by the general formula (1) include

2,5-bis(4-dimethylaminobenzylidene)cyclopentanone,

2,5-bis(4-diethylaminobenzylidene)cyclopentanone,
2,5-bis(4-dibutylaminobenzylidene)cyclopentanone,
2,5-bis[(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolidine-9-yl)methylene]cyclopentanone, 2,5-bis[2-(1,3,3-trimethyl-1,3-dihydro-2(2H)-indolinyli-
dene)ethylidene]cyclopentanone,
2,5-bis[2-(1-ethyl-2(1H)-naphtho[1,2-d]thiazolinyli-
dene)ethylidene]cyclopentanone, 2,5-bis[4-(dimethylamino
cinnamylidene)cyclopentanone, 2,5-bis[4-N-ethyl-N-carbo
methoxymethylaminobenzylidene)cyclopentanone and a sodium salt
thereof, 2,5-bis(4-N-methyl-N-cyanoethylamino
benzylidene)cyclopentanone, 2,5-bis(4-N-ethyl-N-chloro
ethylaminocinnamylidene)cyclopentanone, etc.

However, suitable sensitizing dyes may not be limited thereto.

[0038]

In the case of producing a volume hologram for use requiring high transparency such as an optical element or the like, it is preferable to use a sensitizing dye which decomposes or changes the structure to become transparent by a post-process after hologram recording or a post treatment such as heating, ultraviolet irradiation or the like. As the dye which can be transparent in the post-process or post treatment, there may be mentioned the cyanine dye, the melocyanine dye, the coumarin dye, the ketocoumarin dye and the cyclopentanone dye.

Herein, "transparent" means being visually transparent in the area out of the hologram recording portion or having a

transmittance of 60% or more in the visible region (wavelength of 400 to 700 nm).

[0039]

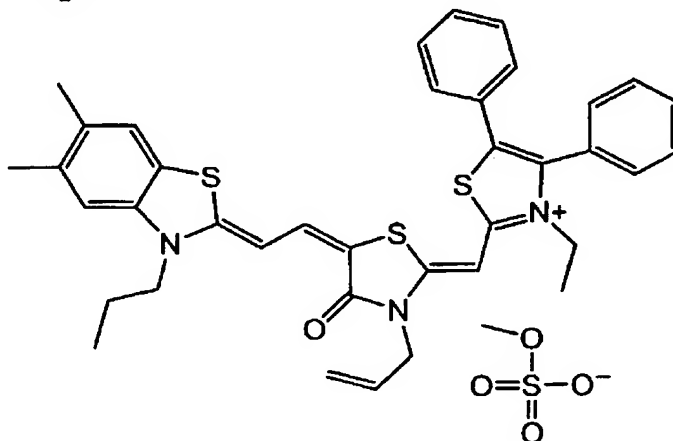
As aforementioned, as the sensitizing dye, one may be used without any limitation if the maximum absorption wavelength deviates from an individually and specifically adopted recording wavelength by 14 nm or more to the high wavelength side or low wavelength side. In relation to the recording wavelength, however, it is particularly preferable to select and use a compound which can highly increase the sensitivity of the composition.

[0040]

For example, as the red recording wavelength, a wavelength at 647.1 nm or 633 nm is often used. In the case of using such a red recording wavelength, particularly, the following compound (1) or (2) is preferably used from the viewpoint of increasing the sensitivity:

[0041]

Compound (1):



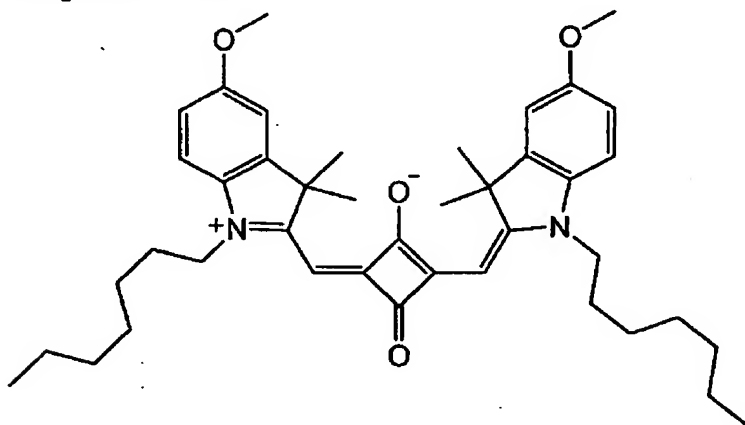
[0042]

Chemical name:

2-[[3-allyl-5-[2-(5,6-dimethyl-3-propyl-2(3H)-benzothiazolylidene)ethylidene]-4-oxo-2-thiazolidinylidene]methyl]-3-ethyl-4,5-diphenylthiazolium methylsulfate
(manufactured by Hayashibara Co., Ltd.);

[0043]

Compound (2):



[0043]

Chemical name:

1-heptyl-2-[3-(1-heptyl-5-methoxy-3,3-dimethyl-1,3-dihydro-indole-2-ylidenemethyl)-2-hydroxy-4-oxo-2-cyclobutenylidenemethyl]-5-methoxy-3,3-dimethyl-3H-indolium inner salt (manufactured by Hayashibara Co., Ltd.)

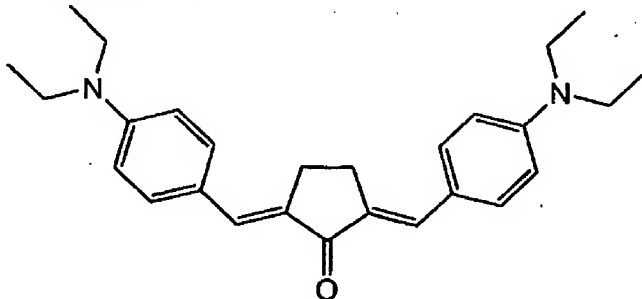
[0045]

Also, as the green recording wavelength, 532 nm, 514.5 nm, 553 nm or 560 nm is often used. In the case of performing interference exposure with the use of such a green recording wavelength, particularly, the following compound (3) or (4) is

preferably used among the cyclopentanone skeleton containing compounds represented by the general formula (1) from the viewpoint of increasing the sensitivity:

[0046]

Compound (3):



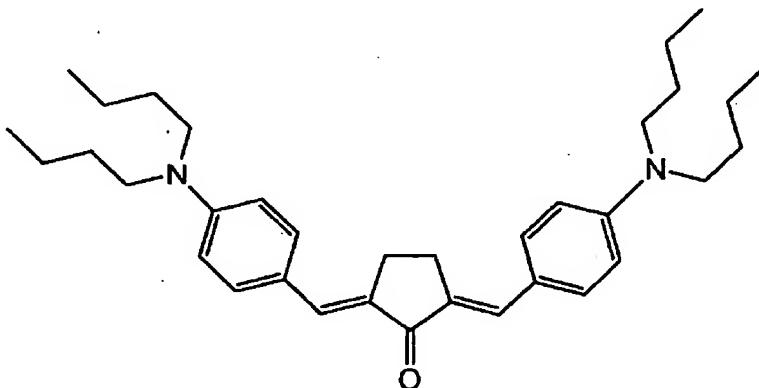
[0047]

Chemical name:

2,5-bis(4-diethylaminobenzylidene)cyclopentanone
(manufactured by Hayashibara Co., Ltd.);

[0048]

Compound (4):



[0049]

Chemical name:

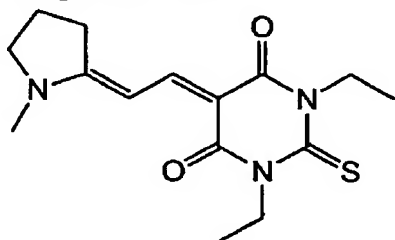
2,5-bis(4-dibutylaminobenzylidene)cyclopentanone
(manufactured by Hayashibara Co., Ltd.)

[0050]

Furthermore, as the blue recording wavelength, 458 nm, 476 nm or 488 nm is often used. In the case of using such a blue recording wavelength, particularly, the following compound (5) or (6) is preferably used among the above exemplified dyes from the viewpoint of increasing the sensitivity:

[0051]

Compound (5):

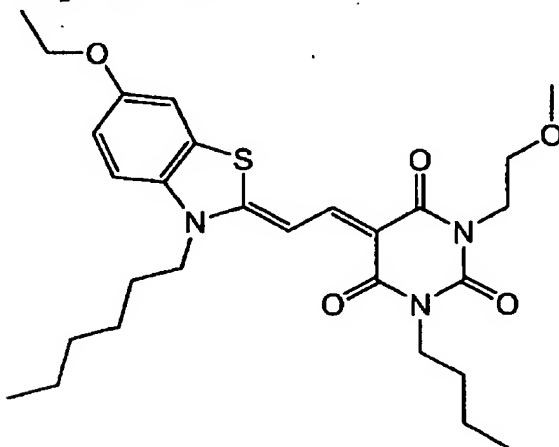


[0052]

Chemical name: 1,3-diethyl-5-[2-(1-methyl-pyrrolidine-2-ylidene)-ethylidene]-2-thioxo-dihydro-pyrimidine-4,6-dione (manufactured by Hayashibara Co., Ltd.);

[0053]

Compound (6):



[0054]

Chemical name:

1-butyl-5-[2-(6-ethoxy-3-hexyl-3H-benzothiazole-
2-ylidene)-ethylidene]-3-(2-methoxy-ethyl)-pyrimidine-
2,4,6-trione (manufactured by Hayashibara Co., Ltd.)

[0055]

The sensitizing dye may be used one kind solely or in
a mixture of two or more kinds.

[0056]

The photopolymerizable compound is a component
(refractive index modulation component) such that when the
hologram recording portion comprising the composition for
hologram recording is subjected to the interference exposure,
the composition is unevenly distributed at high concentration
in a strongly exposed portion due to diffusion movement, and
as a result of being fixed by a polymerization reaction, and
as a result, it causes refractive index modulation at the strongly
exposed portion. By the refractive index modulation, a volume
hologram is recorded.

As the photopolymerizable compound, a compound which can
promote a polymerization or dimerization reaction by light
irradiation and can diffuse and move in the composition for
hologram recording can be used. For example, there may be
mentioned a photopolymerizable compound which can promote a
reaction in the reaction form of, for example, polymerization
reaction such as photoradical polymerization, photocationic
polymerization and photoanionic polymerization, or a

polymerization which proceeds through photodimerization.

[0057]

Among the photopolymerizable compounds, as the photoradical polymerizable compound, a compound which has at least one ethylenically unsaturated bond that is capable of addition-polymerization can be exemplified, the examples of which include unsaturated carboxylic acid and a salt thereof, ester of unsaturated carboxylic acid and aliphatic polyalcohol, ester of unsaturated carboxylic acid and an aromatic skeleton-containing polyalcohol, an amide-bonded compound of unsaturated carboxylic acid and an aliphatic polyvalent amine compound and an amide-bonded compound of unsaturated carboxylic acid and an aromatic skeleton-containing polyvalent amine. Specific examples of a monomer of the ester of unsaturated carboxylic acid and aliphatic polyalcohol compound include ethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, 1,3-butanediol di(meth)acrylate, tetramethyleneglycol di(meth)acrylate, propyleneglycol di(meth)acrylate, neopentylglycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane tri((meth)acryloyloxypropyl)ether, trimethylolethane tri(meth)acrylate, hexanediol di(meth)acrylate, 1,4-cyclohexanediol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol di(meth)acrylate,

dipentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, sorbitol tri(meth)acrylate, sorbitol tetra(meth)acrylate, sorbitol penta(meth)acrylate, sorbitol hexa(meth)acrylate, tri((meth)acryloyloxyethyl) isocyanurate, polyester (meth)acrylate oligomer, 2-phenoxyethyl (meth)acrylate, phenoethoxylate mono(meth)acrylate, 2-(p-chlorophenoxy)ethyl (meth)acrylate, p-chlorophenyl (meth)acrylate, phenyl (meth)acrylate, 2-phenylethyl (meth)acrylate, (2-(meth)acryloxyethyl)ether of bisphenol A, ethoxylated bisphenol A diacrylate, 2-(1-naphthyloxy)ethyl (meth)acrylate, o-biphenyl acrylate, 9,9-bis(4-(meth)acryloxydiethoxyphenyl)fluorene, 9,9-bis(4-(meth)acryloxytriethoxyphenyl)fluorene, 9,9-bis(4-acryloxydipropoxyphenyl)fluorene, 9,9-bis(4-acryloxyethoxy-3-methylphenyl)fluorene, 9,9-bis(4-acryloxyethoxy-3-ethylphenyl)fluorene, 9,9-bis(4-acryloxyethoxy-3,5-dimethyl)fluorene, etc. Also, a sulfur-containing acryl compound disclosed in JP-A No. Sho. 61-72748 can be used, such as 4,4'-bis(β -(meth)acryloyloxyethylthio)diphenylsulfone, 4,4'-bis(β -(meth)acryloyloxyethylthio)diphenylketone, 4,4'-bis(β -(meth)acryloyloxyethylthio)-3,3', 5,5'-tetrabromodiphenylketone, and 2,4-bis(β -(meth)acryloyloxyethylthio)diphenylketone, but may not be limited thereto.

[0057]

Also, among the photopolymerizable compounds, as the photocationic polymerizable compound, there may be mentioned cyclic ethers represented by an epoxy ring and an oxetane ring, thioethers and vinyl ethers. Specific examples of the epoxy ring containing compound include polyalkyleneglycoldiglycidyl ether, bisphenol A diglycidyl ether, glycerin triglycidyl ether, diglycerol triglycidyl ether, diglycidyl hexahydrophthalate, trimethylolpropane diglycidyl ether, allyl glycidyl ether, phenyl glycidyl ether and cyclohexene oxide, but may not be limited thereto.

[0059]

Furthermore, among the photopolymerizable compounds, as the photoanionic polymerizable compound, there may be used a vinyl monomer having electron attractivity, that is, a monomer containing an electron attractive group and having an ethylenically double bond which has anionic polymerization activity increased by the electron attractive group. As such a monomer, for example, there may be mentioned styrene, methyl α -cyanoacrylate, methyl vinyl ketone and acrylonitrile. Also, a monomer which has a chemical structure that can initiate a ring-opening polymerization by an anionic catalyst can be appropriately used as the anionic polymerizable compound, such as cyclic ethers, lactones, lactams, cyclic urethanes, cyclic ureas and cyclic siloxanes.

Among the photopolymerizable compounds, the

photoradical polymerizable compound and the photocationic polymerizable compound are suitably used since many of the photoradical polymerizable compound and the photocationic polymerizable compound are available and easy to control the reaction.

[0060]

When interference exposure is performed on a hologram recording material which contains two or more kinds of refractive index modulation components that have different refractive indexes and rates of diffusion movement involved in a photopolymerization reaction, in the strongly exposed portion,

polymerization reaction of a refractive index modulation component which has a high rate of diffusion movement involved in the photopolymerization reaction preferentially proceeds, and thus the concentration of the refractive index modulation component having a high rate of diffusion movement is increased. At the same time, a refractive index modulation component having a low rate of diffusion movement involved in the photopolymerization reaction is removed from the strongly exposed portion, and diffused and moved to a weakly exposed portion where the refractive index modulation component is polymerized and fixed. As a result, a refractive index difference is generated between the strongly and weakly exposed portions based on the refractive index of each of the different kinds of refractive index modulation components. This is referred to as the volume exclusion effect. The larger the

difference in refractive index, the higher the diffraction efficiency, thereby obtaining a bright hologram.

[0061]

For the purpose of increasing the diffraction efficiency by such a volume exclusion effect, a second refractive index modulation component can be contained in the photosensitive composition for volume hologram recording of the present invention, which has a difference in refractive index from the photopolymerizable compound and increases the distribution of the first refractive index modulation component into the strongly exposed portion by the volume exclusion effect upon interference exposure or increases the difference in refractive index between the strongly and weakly exposed portions.

[0062]

Herein, in the case where the photopolymerizable compound as the first refractive index modulation component is a high refractive index type refractive index modulation component, the photopolymerizable compound is diffused and moved to concentrate in the strongly exposed portion, thereby providing the strongly exposed portion with a high refractive index, while the second refractive index modulation component is removed from the strongly exposed portion and diffused and moved to concentrate in the weakly exposed portion, thereby providing the weakly exposed portion with a low refractive index. On the other hand, in the case that the photopolymerizable compound as the first refractive index modulation component is a low

refractive index type refractive index modulation component, contrary to the above case, the strongly exposed portion is provided with a low refractive index since the concentration of the photopolymerizable compound is increased, and the weakly exposed portion is provided with a high refractive index since the concentration of the second refractive index modulation component is increased.

[0063]

The second refractive index modulation component is for facilitating the refractive index distribution generated by uneven distribution of the photopolymerizable compound as the first refractive index modulation component; therefore, in the case of using both of the second refractive index modulation component and a binder resin, a compound is selected as the second refractive index modulation component, which has a magnitude relation that shows the same tendency as the magnitude relation established between the photopolymerizable compound as the first refractive index modulation component and the binder resin. That is, in the case where the photopolymerizable compound as the first refractive index modulation component is a high refractive index type refractive index modulation component, as the second refractive index modulation component and the binder resin, those that have a lower refractive index than that of the photopolymerizable compound are used. On the other hand, in the case where the photopolymerizable compound as the first refractive index modulation component is a low refractive index

type refractive index modulation component, as the second refractive index modulation component and the binder resin, those that have a higher refractive index than that of the photopolymerizable compound are used. As the second refractive index modulation component, preferred is a compound which has as large a refractive index difference as possible from the photopolymerizable compound used as the first refractive index modulation component.

[0064]

As the second refractive index modulation component, a compound which is selected from the photopolymerizable compounds and has a refractive index difference from the photopolymerizable compound used as the first refractive index modulation component and a lower polymerization rate than that of the same can be used. In this case, the first and second refractive index modulation components can have the same reaction form (for example, both are photoradical polymerizable) or different reaction forms (for example, one is photoradical polymerizable and the other is photocationic polymerizable.) In general, the photocationic polymerizable compound has a lower polymerization rate than that of the photoradical polymerizable compound, so that it is suitable to use a photoradical polymerizable compound as the first refractive index modulation component in combination with a photocationic polymerizable compound as the second refractive index modulation component.

[0065]

Also in the composition for hologram recording of the present invention, a metallic particle can be contained as the second refractive index modulation component, which has a refractive index difference from the photopolymerizable compound as the first refractive index modulation component.

The metallic particle can be an unreactive metallic particle or a polymerization reactive metallic particle having a photopolymerization reactive group or other reactive group introduced on the particle surface, as long as it is a compound which can diffuse and move in a layer of the volume hologram recording material and has a refractive index difference from the photopolymerizable compound.

[0066]

From the viewpoint of diffusing and moving ability in the layer of the composition for hologram recording, the particle diameter of the metallic particle is preferably equal to or smaller than the hologram recording wavelength, specifically 1 to 700 nm, particularly preferably 5 to 500 nm. As a non-photopolymerization reactive metallic particle, for example, there may be mentioned titania, zirconia, zinc, indium and tin.

[0067]

As a method of introducing a photopolymerization reactive group onto the metallic particle, for example, there may be mentioned a method of performing a coupling treatment on the surface of the metallic particle using a photopolymerization

reactive coupling agent by a surface treatment such as a dry method, a wet method and a blend method. Also, as the metallic particle onto which the photopolymerization reactive group is introduced, there may be mentioned a particle of titania, zirconia, zinc, indium, tin or the like as mentioned above. As the photopolymerization reactive group to be introduced, there may be mentioned a polymerizable reaction group which is the same as that of the photopolymerizable compound, that is, a group which can promote a reaction in the reaction form of, for example, polymerization reaction such as photoradical polymerization, photocationic polymerization and photoanionic polymerization, or a polymerization which proceeds through a photodimerization.

[0068]

The photopolymerization initiator is appropriately selected from a photoradical polymerization initiator, a photocationic polymerization initiator, a photoanionic polymerization initiator and the like, depending on the reaction form of the photopolymerizable compound.

[0069]

As the photoradical polymerization initiator, for example, there may be mentioned an imidazole derivative, a bisimidazole derivative, a N-arylglycine derivative, an organic azide compound, titanocenes, an aluminate complex, an organic peroxide, a N-alkoxypyridinium salt, and a thioxanthone derivative. More specifically, for example, there may be mentioned 1,3-di(tert-butyldioxycarbonyl)benzophenone,

3,3',4,4'-tetrakis(tert-butyldioxy carbonyl)benzophenone,
3-phenyl-5-isooxazolone, 2-mercaptobenzoimidazole,
bis(2,4,5-triphenyl)imidazole,
2,2-dimethoxy-1,2-diphenylethane-1-one (product name:
Irgacure 651; manufactured by Ciba Specialty Chemicals, Inc.),
1-hydroxy-cyclohexyl-phenyl-ketone (product name: Irgacure
184; manufactured by Ciba Specialty Chemicals, Inc.),
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butane-1-
on (product name: Irgacure 369; manufactured by Ciba Specialty
Chemicals, Inc.), and bis(η^5 -2,4-cyclopentadiene-1-yl)-bis
(2,6-difluoro-3-(1H-pyrrole-1-yl)-phenyl)titanium
(product name: Irgacure 784; manufactured by Ciba Specialty
Chemicals, Inc.), but may not be limited thereto.

[0070]

As the photocationic polymerization initiator, for
example, there may be mentioned sulfonic ester, imide sulfonate,
dialkyl-4-hydroxysulfonium salt, aryl sulfonate-p-nitrobenzyl
ester, a silanol-aluminum complex, and
(η^6 -benzene)(η^5 -cyclopentadienyl) iron (II). More
specifically, there may be mentioned benzointosilate,
2,5-dinitrobenzyltosilate, N-tosilphthalic imide and the like,
but may not be limited thereto.

As a compound which can be used as the photoradical
polymerization initiator as well as the photocationic
polymerization initiator, there may be mentioned, for example,
an aromatic iodonium salt, an aromatic sulfonium salt, an

aromatic diazonium salt, an aromatic phosphonium salt, a triazine compound, and an iron arene complex. More specifically, for example, there may be mentioned an iodonium salt such as a chloride, bromide, fluoroborate salt, hexafluorophosphate salt, hexafluoroantimonate salt or the like of iodonium such as diphenyliodonium, ditolyliodonium, bis(p-tert-butylphenyl)iodonium, and bis(p-chlorophenyl)iodonium; a sulfonium salt such as a chloride, bromide, fluoroborate salt, hexafluorophosphate salt, hexafluoroantimonate salt or the like of sulfonium such as triphenyl sulfonium, 4-tert-butyltriphenyl sulfonium, and tris(4-methylphenyl) sulfonium; a 2,4,6-substituted-1,3,5 triazine compound such as 2,4,6-tris(trichloromethyl)-1,3,5-triazine, 2-phenyl-4,6-bis(trichloromethyl)-1,3,5-triazine, and 2-methyl-4,6-bis(trichloromethyl)-1,3,5-triazine, but may not be limited thereto.

[0072]

In the case of using such an initiator that functions as both of the photoradical polymerization initiator and the photocationic polymerization initiator, only one kind of photopolymerization initiator is thus contained in the composition for hologram recording, and as the photopolymerizable compound, a photoradical polymerizable compound and a photocationic polymerizable compound can be contained in the composition.

[0073]

As the photoanionic polymerization initiator, for example, there may be mentioned a compound which generates amine by ultraviolet irradiation, more specifically, 1,10-diaminodecane, 4,4'-trimethylenedipiperidine, carbamates and a derivative thereof, a cobalt-amine complex, aminooxyiminos, ammonium borates and the like. As a commercially available product, NBC-101 (product name; manufactured by Midori Kagaku Co., Ltd.) can be exemplified.

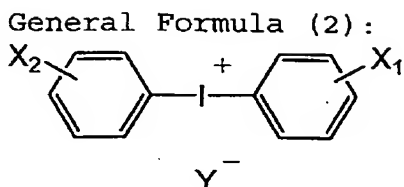
[0074]

From the viewpoint of the stability of a recorded hologram, The photopolymerization initiator is preferably subjected to a decomposition treatment after the hologram recording. For example, an organic peroxide-containing initiator is preferable since the initiator is easily decomposed by ultraviolet irradiation.

[0075]

In the case of using the cyclopentanone skeleton containing compound represented by the aforementioned general formula (1) as the sensitizing dye, it is preferable to use the diaryliodonium salt among the above examples. It is particularly preferable to use the same in combination with a compound containing diaryliodonium skeleton represented by the following general formula (2) since the effect of increasing the sensitivity is high:

[0076]



[0077]

wherein, each of "X₁" and "X₂" is independently an alkyl group having 1 to 20 carbons, halogen or an alkoxy group having 1 to 20 carbons; and "Y⁻" is a monovalent anion.

[0078]

As a specific example of X₁ and X₂, there may be mentioned methyl, ethyl, n-propyl, t-butyl, F, Cl, Br, a methoxy group or the like. As "Y⁻", which is a monovalent anion, any anion which functions as a counter ion can be used, such as I⁻, BF₄⁻, PF₆⁻, SbF₆⁻, CF₃SO₃⁻, AsF₆⁻, or (C₆F₅)₄B⁻.

[0079]

In the composition for hologram recording of the present invention, a binder resin can be contained. By containing the binder resin, a non-flowable volume hologram recording layer can be easily formed on a substrate, and the composition can be utilized as a dry developing type hologram forming material.

[0080]

If the composition for hologram recording of the present invention contains no binder resin and thus has an excessively high flowability, a volume hologram can be recorded in such a manner that a layer of the composition for hologram recording is formed by a suitable method such as inserting the composition between transparent substrates such as glass, followed by

interference exposure, and, if required, the layer is cured by a photo- or heat-curing or other reaction.

[0081]

To increase the diffraction efficiency, it is preferable to use a binder resin having a large refractive index difference from the photopolymerizable compound, which is the refractive index modulation component. The larger the diffraction efficiency, the visually brighter and more excellent the thus-obtained hologram.

[0082]

The binder resin can be or can not be polymerization reactive. However, the binder resin is preferably polymerization reactive since it is possible to increase the physical properties (such as strength and heat resistance) of the coating layer of the photosensitive medium for volume hologram recording or volume hologram formed by using the photosensitive composition for volume hologram recording of the present invention.

[0083]

As the binder resin, a thermoplastic resin can be used. More specifically, there may be used poly(meth)acrylic ester or a partial hydrolyzate thereof, polyvinyl acetate or a hydrolyzate thereof, polyvinyl alcohol or a partially acetalized product thereof, triacetyl cellulose, polyisoprene, polybutadiene, polychloroprene, silicone rubber, polystyrene, polyvinyl butyral, polyvinyl chloride, polyallylate,

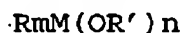
chlorinated polyethylene, chlorinated polypropylene, poly-N-vinylcarbazole or a derivative thereof, poly-N-vinylpyrrolidone or a derivative thereof, a copolymer of styrene and maleic anhydride or a half ester thereof, a copolymer containing at least one polymerization component selected from the group consisting of copolymerizable monomers such as (meth)acrylic acid, (meth)acrylic ester, acrylamide, acrylonitrile, ethylene, propylene, vinyl chloride and vinyl acetate, or a mixture thereof, etc.

[0084]

As the polymerization reactive binder resin, for example, there may be used an organic-inorganic hybrid resin utilizing a sol-gel reaction, or an oligomer type thermosetting resin.

As the organic-inorganic hybrid resin, for example, there may be mentioned an organic-inorganic hybrid polymer such as a copolymer of an organometallic compound having a polymerizable group represented by the following general formula (3) and a vinyl monomer:

General formula (3):



wherein, "M" is a metal selected from the group consisting of Si, Ti, Zr, Zn, In, Sn, Al, Se and the like; "R" is a vinyl group or (meth)acryloyl group having 1 to 10 carbon atoms; "R'" is an alkyl group having 1 to 10 carbon atoms; and "m+n" is the valence of metal "M".

[0085]

As an example of a compound when the metal atom "M" is Si, there may be vinyltriethoxysilane, vinylmethoxysilane, vinyltributoxysilane, vinyltriallyloxysilane, vinyltetraethoxysilane, vinyltetramethoxysilane, (meth)acryloxypropyltrimethoxysilane or the like.

[0086]

As the vinyl monomer used for the organic-inorganic hybrid polymer, there may be mentioned (meth)acrylic acid or (meth)acrylic acid ester, but may not be limited thereto.

[0087]

Among the organic-inorganic hybrid resins, an organometallic compound represented by the following general formula (4) is particularly effective in further increasing the refractive index difference between the binder resin and the photopolymerizable compound since it has a smaller molecular weight than that of the above-mentioned organic-inorganic hybrid polymer which is already polymerized, and it is highly effective in increasing cross-linking density:

General formula (4):



wherein, "M'" is a metal selected from the group consisting of Ti, Zr, Zn, In, Sn, Al, Se and the like; "R'" is an alkyl group having 1 to 10 carbon atoms; and "n'" is the valence of metal "M'".

[0088]

Addition of the organometallic compound represented by

the general formula (4) to the photosensitive composition for volume hologram recording is effective in not only increasing the refractive index of the binder but also increasing the toughness and heat resistance of the layer since the organometallic compound forms a network structure is formed together with the above-mentioned binder resin in the presence of water and an acidic catalyst by a sol-gel reaction. To increase the refractive index difference between the binder resin and the photopolymerizable compound, as metal "M'", a metal having a refractive index as high as possible is preferably used.

[0089]

As the oligomer type thermosetting resin, for example, there may be used a thermosetting epoxy compound produced by a condensation reaction of a phenol compound selected from various kinds of compounds such as bisphenol A, bisphenol S, novolac, o-cresol novolac and p-alkylphenol novolac with epichlorohydrin.

The thermosetting epoxy compound functions as a binder since it is an oligomer which forms a crosslink; moreover, it functions as the second refractive index modulation component since it is photocationic polymerization reactive and has a molecular size that allows the compound to diffuse and move in the composition. Hence, the thermosetting epoxy compound can be contained in the composition for hologram recording instead of other binder resin or together with other binder resin.

[0090]

The hologram recording portion which comprises the photosensitive composition for volume hologram recording that contains the thermosetting epoxy compound, is fixed by a heat treatment after the interference exposure, and the cationic polymerizable compound is crosslinked therewith due to a strong acid produced upon the interference exposure, thereby increasing the refractive index of the portion and thus enhancing the refractive index modulation. Also, due to the resulting crosslinked structure, it is highly effective in increasing mechanical strength and resistance properties such as heat resistance and weather resistance.

[0091]

It is further preferable to use a binder resin which can form a covalent bond with the photoreactive group of the photopolymerizable compound as the binder resin. In this case, after the interference exposure, an unreacted photopolymerizable compound or a polymer of the photopolymerizable compound is connected to the binder resin in the predetermined reaction form by covalent bonding; therefore, a stable bond is produced between the photopolymerizable compound and the binder resin, thereby obtaining a hologram layer which is excellent in layer strength, heat resistance, ability to fix a hologram, etc.

[0092]

It is preferable to introduce a functional group which is photoreactive or thermally polymerizable with the

photoreactive group of the photopolymerizable compound in the binder resin as a functional group which can form the above covalent bond. The hologram recording portion comprising a photopolymer type hologram recording material is often subjected to uniform overall exposure or heating after the process of interference exposure for promoting the refractive index modulation or completing the polymerization reaction. It is preferable that the functional group of the binder resin is capable of photopolymerization or thermal polymerization with the photopolymerizable group of the photopolymerizable compound since the process of exposing or heating all over the hologram recording portion comprising the photosensitive composition for hologram recording after the interference exposure in order to promote refractive index modulation or fix the hologram, and the process of copolymerizing the binder resin with the photopolymerizable compound or a polymer thereof in order to increase the layer strength or resistance of the hologram recording portion, can be combined into one process by a common reaction form.

[0093]

Particularly preferably, a functional group which can photopolymerize with the photoreactive group of the photopolymerizable compound is introduced to the binder resin. For example, in the case where the photopolymerizable compound has an ethylenically unsaturated bond that is capable of addition-polymerization as the photoreactive group, similarly,

a binder resin which has an ethylenically unsaturated bond (preferably, an ethylenic double bond) that is capable of addition-polymerization is used, such as an acryloyl group and a methacryloyl group. In the case where the photopolymerizable compound has a photocationic polymerizable group such as an epoxy group, a binder resin which has a functional group that is polymerizable with the photocationic polymerizable group upon the interference exposure is used. As the functional group that is polymerizable with the photocationic polymerizable group upon the interference exposure includes, besides a photocationic polymerizable group itself such as an epoxy group and a vinyl ether group, a functional group such as a hydroxyl group and a carboxyl group, for example.

[0094]

When the above-mentioned particularly preferable combination is used, the photopolymerizable compound in the strongly exposed portion polymerizes with not only the adjacent photopolymerizable compound but also the peripheral binder resin when the hologram recording portion is subject to the interference exposure. Therefore, there is also an effect that the reactivity of the photopolymerizable compound is increased, and thus the sensitivity of the same to the interference exposure and the amount of refractive index modulation is increased. Also in this case, there is the effect that by performing general and uniform overall exposure or heating after the interference exposure, the refractive index modulation is promoted or the

polymerization reaction is completed so as to form a hologram, and the covalent bonding between the binder resin and the photopolymerizable compound is further developed so as to provide the layer of the hologram recording material with excellent physical properties such as layer strength and heat resistance.

As the binder resin, one kind can be selected from various materials including the above exemplified materials for use, or two or more kinds can be selected for use in combination.

[0095]

If the composition for hologram recording of the present invention contains the binder resin, the sensitizing dye is preferably used in an amount of 0.01 to 20 parts by mass, more preferably 0.01 to 2 parts by mass, with respect to the binder resin of 100 parts by mass.

The photopolymerizable compound is preferably used in an amount of 10 to 1,000 parts by mass, more preferably 10 to 100 parts by mass, with respect to the binder resin of 100 parts by mass.

The photopolymerization initiator is preferably used in an amount of 0.1 to 20 parts by mass, more preferably 5 to 15 parts by mass, with respect to the binder resin of 100 parts by mass.

The thermosetting epoxy compound is preferably used in an amount of 10 to 300 parts by mass, more preferably 70 to 150 parts by mass, with respect to the binder resin of 100 parts by mass.

[0096]

If the composition for hologram recording of the present invention does not contain the binder resin, the compounding amount of each of the sensitizing dye, the photopolymerizable compound, the photopolymerization initiator and the thermosetting epoxy compound can be in the range of the above-mentioned compounding amount of each component with respect to the binder resin of 100 parts by mass.

Also, other than the above components, various additives such as a plasticizer, an adhesion control agent (an adhesion imparting agent) and an antioxidant can be appropriately added to the composition for hologram recording depending on the intended purpose.

By dissolving the above components in acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, benzene, toluene, xylene, chlorobenzene, tetrahydrofuran, methylcellosolve, ethylcellosolve, methylcellosolve acetate, ethylcellosolve acetate, ethyl acetate, 1,4-dioxane, 1,2-dichloroethane, dichloromethane, chloroform, methanol, ethanol, isopropanol or the like, or in a mixed solvent thereof, a coating liquid can be prepared as the composition for hologram recording of the present invention. If the compounding components other than the solvent are also in liquid state at ordinary temperature, the used amount of the coating solvent can be reduced, or there is a case where the coating solvent is not necessary at all.

[0098]

By applying the above-mentioned coating liquid on an appropriate support such as a substrate film by a method such as spin coating, gravure coating, comma coating and bar coating and drying the same, a layer of the photosensitive composition for volume hologram recording (hereinafter, it may be referred to as a hologram recording composition layer) is formed, and a photosensitive medium for volume hologram recording can be thus obtained. A thickness of the hologram recording composition layer is 1 to 100 μm , preferably 2 to 40 μm .

[0099]

If the flowability of the composition for hologram recording is high, the hologram recording portion can be formed by filling a gap formed by disposing a support and a transparent covering material such as a transparent substrate and a plastic film to face each other with the composition for hologram recording.

[0100]

As the substrate film of the photosensitive medium for volume hologram recording, there may be mentioned resins having transparency such as transparent polyester films and polyimide films including a polyethylene film, a polypropylene film, a polyethylene fluoride film, a polyvinylidene fluoride film, a polyvinyl chloride film, a polyvinylidene chloride film, an ethylene-vinyl alcohol film, a polyvinyl alcohol film, a polymethyl methacrylate film, a polyethersulfone film, a

polyether etherketone film, a polyamide film, a tetrafluoroethylene-perfluoroalkylvinyl ether copolymerized film, a polyethylene terephthalate film, etc. The thickness is generally 2 to 200 μm , preferably 10 to 50 μm .

[0101]

If the hologram recording composition layer is adhesive after drying, any of the films exemplified above as the substrate film can be laminated thereto as a protective film. In this case, the contacting surface of the laminated film with the hologram recording composition layer can be subjected to a release treatment so that the film can be easily peeled off from the layer thereafter.

[0102]

The thus-obtained photosensitive medium for volume hologram recording has the hologram recording portion comprising the composition for hologram recording on the support. In general, the hologram recording portion is a hologram recording composition layer having a constant thickness. The hologram recording portion is, however, only needed to be in the form that it is capable of hologram recording; the shape or thickness is not be limited; the thickness is not needed to be constant; and it can be in the form that, as aforementioned, the composition in a fluid state is filled therein.

[0103]

A volume hologram can be formed in the photosensitive medium for volume hologram recording of the present invention

by performing the interference exposure using a conventionally known method.

For example, the photopolymerizable compound is polymerized to some extent by, as needed, preliminarily irradiating the hologram recording material layer of the photosensitive medium for volume hologram recording with relatively weak, uniform light; thereafter, the hologram recording material layer and a hologram original plate are faced and adhered to each other, followed by performing interference exposure from the transparent substrate film side using a recording light in the visible region, thereby forming a volume hologram.

As a light source of the recording light which has high coherence in the visible region, visible laser light is suitable. For example, it is possible to use a laser light that is selected from the group consisting of argon ion laser (458 nm, 488 nm and 514.5 nm), krypton ion laser (647.1 nm), helium-neon ion laser (633 nm), YAG laser (532 nm), Dye laser (553 nm) and so on.

[0104].

In the present invention, a spectral absorption property of the hologram recording portion of the photosensitive medium for volume hologram recording is adjusted in accordance with an individually and specifically determined recording wavelength. That is, a volume hologram recording system can be formed, which comprises the photosensitive medium for volume

hologram recording in which the hologram recording portion comprising the photosensitive composition for volume hologram recording of the present invention is provided on the support, and an optical system in which the hologram recording portion of the photosensitive medium for volume hologram recording is subjected to the interference exposure at a predetermined recording wavelength in the visible region, wherein the sensitizing dye contained in the hologram recording portion has a maximum absorption wavelength deviating by 14 nm or more from the predetermined recording wavelength, and the hologram recording portion itself absorbs at the predetermined recording wavelength.

In the case where the composition for hologram recording of the present invention is used, the recording mechanism is considered to be basically the same as the conventional mechanism. That is, when the hologram recording portion comprising the composition for hologram recording is subjected to the interference exposure, photopolymerization is caused preferentially at a part that is strongly irradiated with light of the hologram recording portion. Accordingly, concentration gradient of the photopolymerizable compound is generated, so that the photopolymerizable compound is diffused and moved from the weakly exposed portion to the strongly exposed portion. As a result, in accordance with the intensity of the interferential light, the photopolymerizable compound has a difference in density, resulting in a difference in refractive index.

[0106]

Herein, in the case where the composition for hologram recording contains the binder resin, after the hologram recording portion is subjected to the interference exposure, the concentration of the binder resin becomes high in the weakly exposed portion, and the refractive index approaches that of the binder resin itself. On the other hand, the concentration of the photopolymerizable compound or a polymer thereof becomes high in the strongly exposed portion, and the refractive index approaches that of the photopolymerizable compound itself. Accordingly, if the refractive index of the photopolymerizable compound is higher than that of the binder resin, the refractive index increases at the part having a higher exposure intensity. If the refractive index of the photopolymerizable compound is lower than that of the binder resin, the refractive index decreases at the part having a higher exposure intensity. The difference in refractive index becomes an interference fringe; therefore, a volume hologram is formed.

[0107]

In the present invention, it is presumed that by using the sensitizing dye which has a maximum absorption wavelength deviating from a recording wavelength by 14 nm or more in such a hologram recording mechanism, there is a significant increase in the possibility of exciting the sensitizing dye to an appropriate energy level at which activation energy can be easily and more effectively transmitted to the initiator, thereby

obtaining excellent sensitivity and hologram recording performance.

As a result, diffraction efficiency can be increased and a visually bright, excellent hologram can be formed.

[0108]

Furthermore, it is preferable to perform one or more treatments in an appropriate order as needed after the interference exposure, which are selected from the group consisting of an expansion treatment for the purpose of tuning the hologram reproducing wavelength or making a peak diffraction wavelength wider in a transmittance curve, overall exposure to uniform light irradiation, and a heat treatment, so that polymerization reaction of an unreacted photopolymerizable compound can be promoted, and the refractive index modulation amount (Δn) can be increased; moreover, the photopolymerization initiator and the sensitizing dye are dereactivated, thereby increasing the resistance properties of the volume hologram such as heat resistance and moisture resistance.

[0109]

The uniform light irradiation after the interference exposure is not needed to be in the visible light region and can be ultraviolet light. It is, for example, performed by means of a light source such as a super high-pressure mercury lamp, a high-pressure mercury lamp, a carbon arc, a xenon arc and a metal halide lamp, generally at a total exposure amount of about 0.1 to 10,000 mJ/cm², preferably 10 to 4,000 mJ/cm².

If the heat treatment is performed after the interference exposure, the heat treatment is performed instead of the uniform light irradiation, or before or after the uniform light irradiation. By the heat treatment, phase separation is promoted, and an unpolymerized photoreactive component in the photosensitive composition for hologram recording is diffused and moved to complete the polymerization; therefore, the refractive index modulation amount (Δn) is increased, and the photosensitive composition for hologram recording is fixed. Also, since the solvent vaporizes, the refractive index modulation amount (Δn) is further increased, and as well as overall exposure to ultraviolet light, the resistance properties of the volume hologram such as heat resistance and moisture resistance can be increased. The heat treatment is generally performed at 40°C to 150°C, preferably 40°C to 100°C, and generally for 5 to 120 minutes, preferably 5 to 30 minutes.

As described above, the hologram recording portion of the photosensitive medium for hologram recording generates the interference fringe by the interference exposure to form a hologram, thereby obtaining a volume hologram. According to the present invention, a volume hologram having a diffraction efficiency of 80% or more, preferably 90% or more, is produced.

Examples

Next, the present invention will be explained with

reference to Examples.

[0112]

1. Production of a volume hologram

(Example 1)

(1) Preparation of a photosensitive composition for volume hologram recording

The following components were mixed to obtain a photosensitive composition for volume hologram recording.

<Composition>

·Polyvinyl acetate (manufactured by Sowa Kagaku K. K.; weight average molecular weight: 100,000): 100 parts by mass

·9,9-Bis(4-acryloxydiethoxyphenyl)fluorene (product name: BPEFA; manufactured by Osaka Gas Co., Ltd.): 80 parts by mass

·Diaryliodonium salt (product name: PI2074; manufactured by Rhodia): 5 parts by mass

·2-[[[3-allyl-5-[2-(5,6-dimethyl-3-propyl-2(3H)-benzothiazolylylidene)ethylidene]-4-oxo-2-thiazolidinylylidene]methyl]-3-ethyl-4,5-diphenylthiazolium methylsulfate (the aforementioned compound (1); manufactured by Hayashibara Co., Ltd; the maximum absorption wavelength (λ_{MAX}): 602.5 nm): 1 part by mass

·1,6-Hexanediol diglycidyl ether (product name: EX-212; manufactured by Nagase Chemtex Corporation): 70 parts by mass

·Toluene: 30 parts by mass

Methyl ethyl ketone: 30 parts by mass

[0113]

(2) Production of a photosensitive medium for volume hologram recording

The photosensitive composition for volume hologram recording was applied on a polyethyleneterephthalate (hereinafter referred to as "PET") film (product name: Lumirror T-60; manufactured by Toray Industries, Inc.) having a thickness of 50 μm by means of a bar coater to form a hologram recording composition layer having a thickness of 10 μm after drying, thereby producing a photosensitive medium for volume hologram recording.

[0114]

(3) Production of a volume hologram

The hologram recording composition layer side of the photosensitive medium for volume hologram recording was laminated onto a mirror. Interference exposure was performed by krypton ion laser light of 647.1 nm entering from the PET film side, thereby recording a volume hologram.

Next, an interference fringe was fixed by heating and ultraviolet irradiation to obtain a volume hologram.

[0115]

(Example 2)

A volume hologram was produced under the same condition as Example 1 except that the composition of the photosensitive composition for volume hologram recording was changed to the

following:

<Composition>

•Polyvinyl acetate (manufactured by Sowa Kagaku K. K.; weight average molecular weight: 100,000): 100 parts by mass

•9,9-Bis(4-acryloxydiethoxyphenyl)fluorene (product name: BPEFA; manufactured by Osaka Gas Co., Ltd.): 80 parts by mass

•Diaryliodonium salt (product name: PI2074; manufactured by Rhodia): 5 parts by mass

•1-Heptyl-2-[3-(1-heptyl-5-methoxy-3,3-dimethyl-1,3-dihydro-indole-2-ylidenemethyl)-2-hydroxy-4-oxo-2-cyclobutenylidenemethyl]-5-methoxy-3,3-dimethyl-3H-indolium inner salt (the above-mentioned compound(2); manufactured by Hayashibara Co., Ltd.; λ_{MAX} : 662 nm): 1 part by mass

•1,6-Hexanediol diglycidyl ether (product name: EX-212; manufactured by Nagase Chemtex Corporation): 70 parts by mass

•Toluene: 30 parts by mass

•Methyl ethyl ketone: 30 parts by mass

[0116]

(Example 3)

A volume hologram was produced under the same condition as Example 1 except that the composition of the photosensitive composition for volume hologram recording was changed to the following, and the light source for hologram recording was changed to YAG laser light of 532 nm.

<Composition>

·Polyvinyl acetate (manufactured by Sowa Kagaku K. K.; weight average molecular weight: 100,000): 100 parts by mass

·9,9-Bis(4-acryloxydiethoxyphenyl)fluorene
(product name: BPEFA; manufactured by Osaka Gas Co., Ltd.): 80 parts by mass

·Diaryliodoniumsalt (product name: PI2074; manufactured by Rhodia): 5 parts by mass

·2,5-Bis(4-diethylaminobenzylidene)cyclopentanone
(the above-mentioned compound (3); manufactured by Hayashibara Co., Ltd.; the maximum absorption wavelength (λ_{MAX}): 479.5 nm): 1 part by mass

·1,6-Hexanediol diglycidyl ether (product name: EX-212; manufactured by Nagase Chemtex Corporation): 70 parts by mass

·Toluene: 30 parts by mass

·Methyl ethyl ketone: 30 parts by mass

[0117]

(Example 4)

A volume hologram was produced under the same condition as Example 1 except that the composition of the photosensitive composition for volume hologram recording was changed to the following, and the light source for hologram recording was changed to YAG laser light of 532 nm.

<Composition>

·Polyvinyl acetate (manufactured by Sowa Kagaku K. K.; weight average molecular weight: 100,000): 100 parts by mass

·9,9-Bis(4-acryloxydiethoxyphenyl)fluorene

(product name: BPEFA; manufactured by Osaka Gas Co., Ltd.): 80 parts by mass

•Diaryliodonium salt (product name: PI2074; manufactured by Rhodia): 5 parts by mass

•2,5-Bis(4-dibutylaminobenzylidene)cyclopentanone (the above-mentioned compound (4); manufactured by Hayashibara Co., Ltd.; the maximum absorption wavelength (λ_{MAX}): 483 nm): 1 part by mass

•1,6-Hexanediol diglycidyl ether (product name: EX-212; manufactured by Nagase Chemtex Corporation): 70 parts by mass

•Toluene: 30 parts by mass

•Methyl ethyl ketone: 30 parts by mass

[0118]

(Example 5)

A volume hologram was produced under the same condition as Example 1 except that the composition of the photosensitive composition for volume hologram recording was changed to the following, and the light source for hologram recording was changed to argon ion laser light of 458 nm.

<Composition>

•Polyvinyl acetate (manufactured by Sowa Kagaku K. K.; weight average molecular weight: 100,000): 100 parts by mass

•9,9-Bis(4-acryloxydiethoxyphenyl)fluorene (product name: BPEFA; manufactured by Osaka Gas Co., Ltd.): 80 parts by mass

•Diaryliodonium salt (product name: PI2074; manufactured

by Rhodia): 5 parts by mass

·1,3-Diethyl-5-[2-(1-methyl-pyrrolidine-2-ylidene)-ethylidene]-2-thioxo-dihydro-pyrimidine-4,6-dione (the above-mentioned compound (5); manufactured by Hayashibara Co., Ltd.; the maximum absorption wavelength (λ_{MAX}): 437.5 nm): 1 part by mass

·1,6-Hexanediol diglycidyl ether (product name: EX-212; manufactured by Nagase Chemtex Corporation): 70 parts by mass

·Toluene: 30 parts by mass

·Methyl ethyl ketone: 30 parts by mass

[0119]

(Example 6)

A volume hologram was produced under the same condition as Example 1 except that the composition of the photosensitive composition for volume hologram recording was changed to the following, and the light source for hologram recording was changed to argon ion laser light of 458 nm.

<Composition>

·Polyvinyl acetate (manufactured by Sowa Kagaku K. K.; weight average molecular weight: 100,000): 100 parts by mass

·9,9-Bis(4-acryloxydiethoxyphenyl)fluorene (product name: BPEFA; manufactured by Osaka Gas Co., Ltd.): 80 parts by mass

·Diaryliodonium salt (product name: PI2074; manufactured by Rhodia): 5 parts by mass

·1-Butyl-5-[2-(6-ethoxy-3-hexyl-3H-benzothiazole-2-

ilidene)-ethylidene]-3-(2-methoxy-ethyl)-pyrimidine-2,4,6-trione (the above-mentioned compound(6); manufactured by Hayashibara Co., Ltd.; the maximum absorption wavelength (λ_{MAX}): 489.5 nm): 1 part by mass

·1,6-Hexanediol diglycidyl ether (product name: EX-212; manufactured by Nagase Chemtex Corporation): 70 parts by mass

·Toluene: 30 parts by mass

·Methyl ethyl ketone: 30 parts by mass

[0120]

(Comparative example 1)

An attempt was made to produce a volume hologram under the same condition as Example 1 except that the composition of the photosensitive composition for volume hologram recording was changed to the following. However, no interference fringe was recorded by the photopolymerizable compound since the initiator was not sufficiently activated for recording by the sensitizing dye, thereby failing to produce a hologram.

<Composition>

·Polyvinyl acetate (manufactured by Sowa Kagaku K. K.; weight average molecular weight: 100,000): 100 parts by mass

·9,9-Bis(4-acryloxydiethoxyphenyl)fluorene
(product name: BPEFA; manufactured by Osaka Gas Co., Ltd.): 80 parts by mass

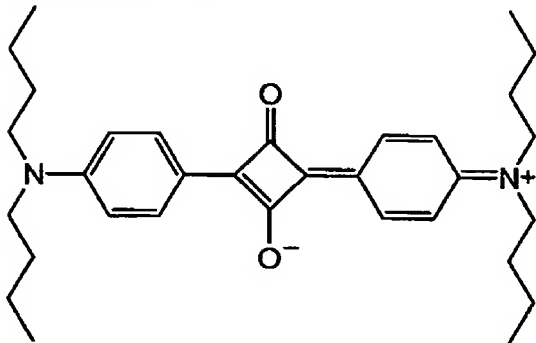
·Diaryliodonium salt (product name: PI2074; manufactured by Rhodia): 5 parts by mass

·Dibutyl-{4-[3-(4-dibutylamino-phenyl)-2-hydroxy-

4-oxo-2-cyclobutenylidene]-cyclohexa-2,5-dienylidene}-ammonium inner salt (a compound (7) represented by the following formula; manufactured by Hayashibara Co., Ltd.; the maximum absorption wavelength (λ_{MAX}): 649 nm): 1 part by mass

[0121]

Compound (7):



[0122]

•1,6-Hexanediol diglycidyl ether (product name: EX-212; manufactured by Nagase Chemtex Corporation): 70 parts by mass

•Toluene: 30 parts by mass

•Methyl ethyl ketone: 30 parts by mass

[0123]

(Comparative example 2)

An attempt was made to produce a volume hologram under the same condition as Example 1 except that the composition of the photosensitive composition for volume hologram recording was changed to the following, and the light source for hologram recording was changed to YAG laser light of 532 nm. However, no interference fringe was recorded by the photopolymerizable compound since the initiator was not sufficiently activated for recording by the sensitizing dye, thereby failing to produce

a hologram.

<Composition>

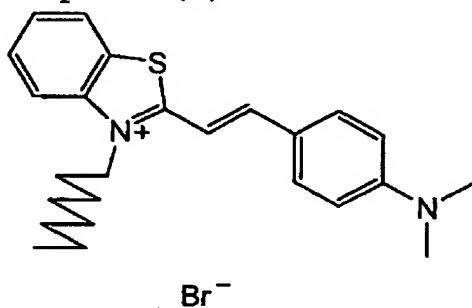
•Polyvinyl acetate (manufactured by Sowa Kagaku K. K.; weight average molecular weight: 100,000): 100 parts by mass

•9,9-Bis(4-acryloxydiethoxyphenyl)fluorene (product name: BPEFA; manufactured by Osaka Gas Co., Ltd.): 80 parts by mass

•Diaryliodonium salt (product name: PI2074; manufactured by Rhodia): 5 parts by mass

•2-[2-(4-dimethylamino-phenyl)-vinyl]-3-octyl-3-benzothiazolium bromide (a compound (8) represented by the following formula; manufactured by Hayashibara Co., Ltd.; the maximum absorption wavelength (λ_{MAX}): 528 nm): 1 part by mass [0124]

Compound (8):



[0125]

•1,6-Hexanedioldiglycidylether (product name: EX-212; manufactured by Nagase ChemteX Corporation): 70 parts by mass

•Toluene: 30 parts by mass

•Methyl ethyl ketone: 30 parts by mass

[0126]

(Comparative example 3)

An attempt was made to produce a volume hologram under the same condition as Example 1 except that the composition of the photosensitive composition for volume hologram recording was changed to the following, and the light source for hologram recording was changed to argon ion laser light of 458 nm. However, no interference fringe was recorded by the photopolymerizable compound since the initiator was not sufficiently activated for recording by the sensitizing dye, thereby failing to produce a hologram.

<Composition>

•Polyvinyl acetate (manufactured by Sowa Kagaku K. K.; weight average molecular weight: 100,000): 100 parts by mass

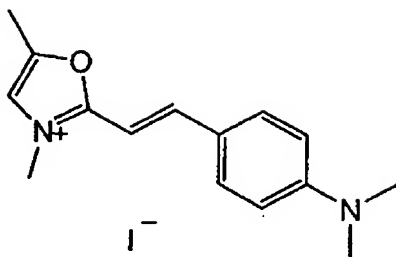
•9,9-Bis(4-acryloxydiethoxyphenyl)fluorene
(product name: BPEFA; manufactured by Osaka Gas Co., Ltd.): 80 parts by mass

•Diaryliodonium salt (product name: PI2074; manufactured by Rhodia): 5 parts by mass

•2-[2-(4-dimethylamino-phenyl)-vinyl]-3,5-dimethyl-3-oxazolium iodide (a compound (9) represented by the following formula; manufactured by Hayashibara Co., Ltd.; the maximum absorption wavelength (λ_{MAX}): 459 nm): 1 part by mass

[0127]

Compound (9):



[0128]

•1,6-Hexanediol diglycidyl ether (product name: EX-212; manufactured by Nagase Chemtex Corporation): 70 parts by mass

•Toluene: 30 parts by mass

•Methyl ethyl ketone: 30 parts by mass

[0129]

2. Evaluation of hologram recording performance

(1) The maximum absorption wavelength of sensitizing dye and absorption of composition at recording wavelength

The photosensitive composition for volume hologram recording obtained in each Example or Comparative example was applied on a PET film having a thickness of 50 μm (product name: Lumirror T-60; manufactured by Toray Industries, Inc.) to form a hologram recording composition layer having a thickness of 10 μm after drying. Thereafter, the maximum absorption wavelength of the sensitizing dye was measured by means of a spectrometer (product name: UVPC-3100; manufactured by Shimadzu Corporation). At the same time, it was confirmed if the hologram recording composition layer absorbs at the recording wavelength.

[0130]

(2) Diffraction efficiency

Transmittance was measured by means of a spectrometer (product name: UVPC-3100; manufactured by Shimadzu Corporation) to calculate diffraction efficiency $\eta = |A-B|/B$ wherein the peak transmittance and base transmittance of the thus-obtained spectral transmittance curve are "A" and "B", respectively (see FIG. 1).

[0131]

(3) Evaluation results

Table 1 shows the diffraction efficiency of each of the volume holograms produced in Examples and Comparative examples, together with the recording wavelength, the sensitizing dye, the maximum absorption wavelength (λ_{MAX}) of the sensitizing dye, the difference between the recording wavelength and λ_{MAX} , and the presence of absorption at the recording wavelength by each composition.

In all Examples, a bright hologram having a high diffraction efficiency was obtained. In all Comparative examples, however, a hologram could not be produced since the initiator was not sufficiently activated for recording by the sensitizing dye.

[0132]

Table 1

	Recording wavelength (nm)	Sensitizing dye		Difference between recording wavelength and λ_{MAX}	Hologram recording	Diffraction efficiency η (%)
		Dye	Maximum absorption wavelength λ_{MAX} (nm)			
Example 1	Red (647.1)	Compound(1)	602.5	44.6		
Example 2		Compound(2)	662	14.9	o (Yes)	96
Example 3	Green (532)	Compound(3)	479.5	52.5	o (Yes)	93
Example 4		Compound(4)	483	49	o (Yes)	88

Example 5	Blue (458)	Compound(5)	437.5	20.5	o (Yes)	86
Example 6		Compound(6)	489.5	31.5	o (Yes)	57
Comparative example 1	Red (647.1)	Compound(7)	649	1.9	o (Yes)	60
Comparative example 2	Green (532)	Compound(8)	528	4	x (No)	—
Comparative example 3	Blue (458)	Compound(9)	459	1	x (No)	—

Brief Description of Drawing

[0133]

In the accompanying drawing,

FIG. 1 is a graph showing a method of calculating diffraction efficiency.

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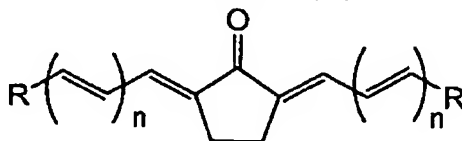
CLAIMS

1. A photosensitive composition for volume hologram recording comprising a photopolymerizable compound as a refractive index modulation component, a photopolymerization initiator and a sensitizing dye which increases the sensitivity of the photopolymerization initiator with respect to a wavelength in the visible region, wherein the sensitizing dye has a maximum absorption wavelength deviating by 14 nm or more from a predetermined volume hologram recording wavelength in the visible region, and the composition itself absorbs at the predetermined volume hologram recording wavelength.

2. The photosensitive composition for volume hologram recording according to Claim 1, wherein a binder resin and/or a thermosetting compound is further contained.

3. The photosensitive composition for volume hologram recording according to Claim 1 or 2, wherein the sensitizing dye is a cyclopentanone skeleton containing compound represented by the following general formula (1):

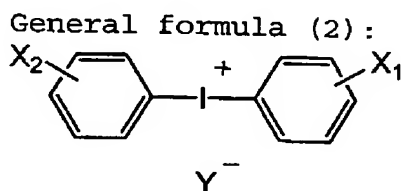
General formula (1):



wherein, "R" is a carbon-nitrogen containing substituent represented by "N_xC_y" in which x=1 to 4, y=8 to 30; "R" may contain

a hydrogen atom and/or a halogen atom; and "n" is an integer of 0 to 3.

4. The photosensitive composition for volume hologram recording according to any of Claims 1 to 3, wherein the photopolymerization initiator is a compound containing diaryliodonium skeleton represented by the following general formula (2):



wherein, each of "X₁" and "X₂" is independently an alkyl group having 1 to 20 carbons, halogen or an alkoxy group having 1 to 20 carbons; and "Y⁻" is a monovalent anion.

5. The photosensitive composition for volume hologram recording according to any of Claims 1 to 4, wherein the photopolymerizable compound is at least one kind selected from the group consisting of a photoradical polymerizable compound and a photocationic polymerizable compound.

6. The photosensitive composition for volume hologram recording according to any of Claims 1 to 5, wherein the photosensitive composition for volume hologram recording further contains a second refractive index modulation component having a different refractive index from that of the

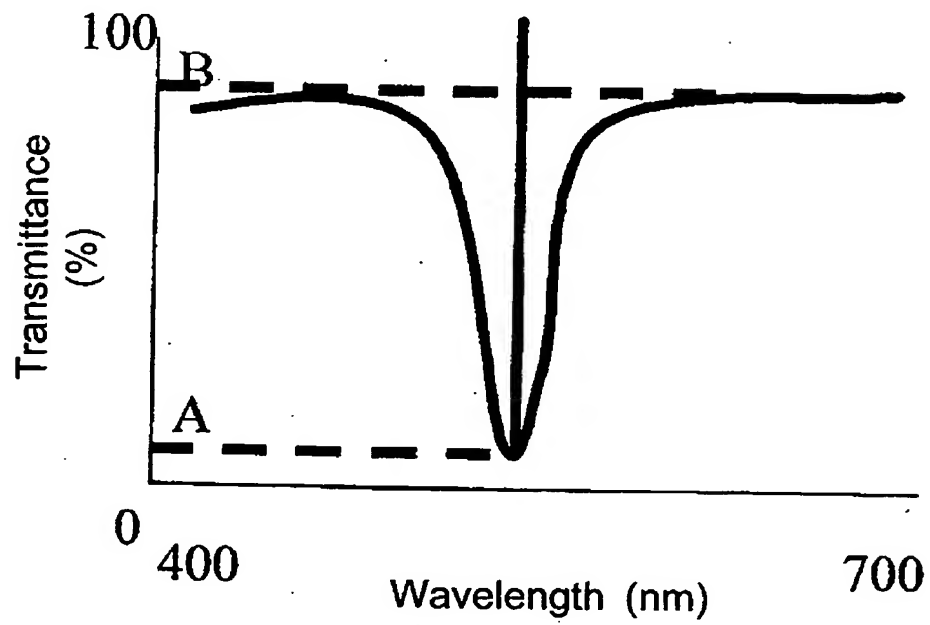
photopolymerizable compound.

7. The photosensitive composition for volume hologram recording according to any of Claims 1 to 6, wherein the sensitizing dye has a maximum absorption wavelength deviating by 14 nm or more from a predetermined volume hologram recording wavelength in the region of 514 nm to 560 nm.

8. The photosensitive composition for volume hologram recording according to any of Claims 1 to 7, wherein a volume hologram having a diffraction efficiency of 80% or more is obtained.

FIG. 1

Calculation of Diffraction Efficiency



ABSTRACT

An object of the present invention is to provide a volume hologram recording material wherein the composition is adjusted in accordance with an individually and specifically determined recording wavelength in the visible region, and is excellent in sensitivity or hologram recording performance. This object was achieved by a photosensitive composition for volume hologram recording comprising a photopolymerizable compound, a photopolymerization initiator and a sensitizing dye, wherein the sensitizing dye has a maximum absorption wavelength deviating by 14 nm or more from a predetermined volume hologram recording wavelength in the visible region, and the composition itself absorbs at the predetermined volume hologram recording wavelength.